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(54) **Selective metallisation of insulating substrates by printing surface with carbon-based ink catalyst and electroless and electrolytic plating**

(57) A process for metal deposition on selected areas of an electrically insulating surface eg. in producing PBC comprises covering the selected areas with carbon based inks prior to the metal deposition process using any process known in the existing art of printing eg. impact, non-impact, xerographic, electrostatic printing. The metallization process consists of the steps of cleaning the surface after printing, optional sensitisation of the surface after cleaning, electroless deposition of the metal and electrolytic deposition of the same or another metal until a desired thickness or finish has been obtained.

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TITLE

Process for Selective Metallization on Insulating Surfaces

This invention relates to a process for selective metallization on insulating surfaces. Metallization of non-conductors is an effective way to render conductivity to insulators without incurring the weight and cost of the bulk metal. It is also occasionally used to impart metallic sheen and lustre to an otherwise unappealing look of the plastics. Depending on the applications, the metal layer can vary in thickness from 0.5 µm to 40 µm. Metallization can be carried out by physical means such as vapour deposition or coating the surface with a conductive ink, or by chemical methods which sensitise the surface for selective chemical deposition of the metal. The cost associated with the physical methods of deposition is relatively high and as such the methods are limited to applications that do not call for heavy build up of thickness. In contrast, the chemical methods are more adaptable to engineering applications that require sufficiently thick deposits of the metal, e.g. metallization of selected areas on a printed-circuit board (PBC). The process involves invariably many steps

in which a conductive metal is to be formed upon selective areas of an insulating surface. The current state of the art consists of multiple steps that begin with the generation of selected areas for metal deposition on the insulating surface by photochemical reactions, the use of palladium-tin colloidal systems to sensitise the selected areas, the decomposition of the palladium-tin colloids by an activating agent, (for example a mild acid) to form an adherent layer of palladium metal that acts as catalyst in the ensuing electroless copper deposition. The cost of such procedure depends on the metallization area, and could be prohibitive if the coverage by metal on the surface is extensive.

The present invention relates to an alternative means to achieve the same end results using a much simplified method and less expensive raw materials.

According to this invention there is provided a process for electroplating graphic patterns on to an insulating surface comprising the steps of transferring the desired patterns to the insulating surface using a carbon based ink, selective deposition of metal on the printed areas by means of electroless deposition, and thereafter depositing electrolytically a similar metal, a dissimilar metal, or multiple metals to the desired

thickness.

Preferably the patterns are printed using an impact, non-impact, electrostatic or xerographic method, or other known techniques of the printing art.

The insulating surface may be subject to a treatment after printing, such as a washing and rinsing process and before metal deposition onto the printed areas.

Advantageously and after electrolytic deposition a finishing process is applied, optionally followed by application of a protective coating.

Preferably the metal used in the initial electroless deposition on the insulating surfaces includes alone or in any combination copper, nickel, silver and/or gold.

The formation of metallization patterns on the insulating surface makes use of printing methods instead of photochemistry. The use of palladium-tin colloidal systems is unnecessary as the catalyst for electroless metal deposition comes from the carbon in the print. The invention is most adaptable to the metallization of graphic patterns on flexible substrate both for engineering and decorative applications. The following sections will describe, by means of illustrations, the metallization of graphic patters on a flexible transparent film typically made of polyethylene terphthalate (PET), as exemplary of one of the many steps

in the production of flexible electrical circuits.

In this invention the graphic pattern to be transferred to the insulating surface is produced by a variety of means known generally from the existing art. The original artwork of the pattern can be enlarged or reduced from the master film according to the size requirement of the final image. The final image is printed on the insulating surface with a carbon based ink following established procedures known in the printing art encompassing both impact and non-impact methods. Details specific to the method such as the preparation of print plates and ancillary equipment, the treatment of the printing surface, and the application of the ink will be provided by the current knowledge in that particular art. The rate of subsequent metallization by electroless deposition depends on the quality of carbon in the ink, with the conductive form of the carbon producing the fastest results. The printed film may also undergo specific surface treatment as described herein to accelerate the deposition process if a less satisfactory ink is used. However, the use of palladium-tin colloids is totally unnecessary in such surface treatment. The carbon in the print suffices as a catalyst in the electroless deposition of copper, silver, nickel and gold and hence only those areas

imprinted with the pattern will be rendered conductive by selective metal deposition. After a sufficient thickness is obtained, electrolytic deposition of a similar or dissimilar metal can be used to build up the thickness at a low cost. Subsequent finishing procedure for the metal electroplate, if necessary, then follows the accepted practice in the art.

EXAMPLE

The following is a description, by way of example only, of a particular application of this invention for the production of metallized graphic patterns on a polyethylene terphthalate (PET) based film.

In the method of this invention the artwork of the electrical circuit is transferred to the PET based film by means of a xerographic process. The film after xerography is treated by an alcoholic KOH wash followed by a deionised water rinse. The thoroughly cleansed film is then immersed with the printed face up in a suitable electroless copper solution. The following formulation known from the art was used in the example.

$CuSO_4 5H_2 0$	7.5 g/l
Rochelle salt	85 g/l
Na_2CO_3	15 g/l
NaOH	12 g/l
Formalin solution, 37% by weight	36 ml/l
Working temperature	room temperature

Depending on the quality of the carbon in the ink, the printed area will be covered by copper deposit visible to the naked eye in 10 minutes to 12 hours. An unstabilised copper electroless solution may undergo non-catalytic decomposition after 12-16 hours. The copper deposited by such non-catalytic process, which may cover

the film in non-printed areas as well, will not adhere strongly to the film, and hence can be easily removed by a simple rinsing operation. Only the copper deposited catalytically upon the presence of the carbon in the printed area will remain adherent and suitable for subsequent build up of thickness by electrolytic methods. As and when it is necessary, electroplating of a similar, a dissimilar, or multiple metals can then proceed according to the existing art including all the necessary pre- and post- treatment of the surfaces for a good finished product. A clear lacquer compatible with the film material can also be applied to the final product for protection against aerial oxidation.

The rate of catalytic copper deposition can be accelerated by treating the film after xerography in the following sequence: an initial alcoholic KOH wash, deionised water rinse, an activation by 0.01M $AgNO_3$ in 4M HNO_3, and a final cleansing in deionised water. A slower electroless copper formulation may need to be used to moderate the rate of copper deposition, as too rapid deposition of copper may encapsulate impurities from the reaction products, reducing the chemical and physical uniformity in the electroless copper deposit.

CLAIMS

1. A process for electroplating graphic patterns on to an insulating surface comprising the steps of transferring the desired patterns to the insulating surface using a carbon based ink, selective deposition of metal on the printed areas by means of electroless deposition, and thereafter depositing electrolytically a similar metal, a dissimilar metal, or multiple metals to the desired thickness.

2. A process in accordance with Claim 1, wherein the patterns are printed using an impact, non-impact, electrostatic or xerographic method, or other known techniques of the printing art.

3. A process in accordance with Claim 1 or 2, wherein the insulating surface is subject to a treatment after printing, such as a washing and rinsing process and before metal deposition onto the printed areas.

4. A process in accordance with any preceding claim, wherein after electrolytic deposition a finishing process is applied, optionally followed by application of a protective coating.

5. A process in accordance with any preceding claim, wherein the metal used in the initial electroless deposition on the insulating surfaces includes alone or in any combination copper, nickel, silver and/or gold.

6. A process for selectively metallizing insulating surfaces substantially as described herein and exemplified.

7. An insulating article, surface or substrate to which a metal layer has been applied using a method as hereinbefore claimed or disclosed. '